

Adsorption of HO<sub>x</sub> on Aerosol Surfaces: Implications for the Atmosphere of Mars

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The potential impact of heterogeneous chemistry on the abundance and distribution of HO<sub>x</sub> in the atmosphere of Mars has been assessed by combining observational data of dust and ice aerosol distributions with an updated photochemical model. Critical parameters include the altitude distributions of aerosols, and the surface loss coefficients ( $\gamma$ ) of HO<sub>2</sub> on dust and ice in the lower atmosphere, and H on ice above 40 km. We find that adsorption of HO<sub>2</sub> on dust ( $\gamma_{\text{HO}_2} \geq 0.01$ ), or ice near 30 km ( $\gamma_{\text{HO}_2} \geq 0.1$ ), can deplete OH abundances in the lower atmosphere by 10% or more. Such depletions approach those obtained by lowering the water vapor abundance by an order of magnitude below the global average observed by Viking ( $\approx 25\%$ ). Since the oxidation of CO is catalyzed by HO<sub>x</sub> in the lower atmosphere via the reaction  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ , loss of OH due to adsorption of HO<sub>2</sub> on dust or ice at low altitudes could have a significant effect on the ratio CO : CO<sub>2</sub>. The adsorption of H on ice at 50 km ( $\gamma_{\text{H}} \geq 0.01$ ) can result in even larger OH depletions. However, this effect is localized to altitudes  $> 40$  km, where CO oxidation is relatively unimportant. Laboratory data suggest that  $\gamma_{\text{HO}_2} \approx 0.01$  is a reasonable estimate for adsorption on dust. Larger values are plausible, but are not strongly supported by experimental evidence. The reactivity of HO<sub>2</sub> on ice is unknown, while  $\gamma_{\text{H}}$  on ice appears to be  $< 0.001$ . There is a need for measurements of HO<sub>x</sub> adsorption on surfaces representative of Martian aerosols at temperatures  $< 220$  K.

## INTRODUCTION

Carbon dioxide comprises over 95% of the atmosphere of Mars, despite continuous photolysis of CO<sub>2</sub> by solar UV radiation. Since the direct recombination of CO and O is slow, the balance between CO<sub>2</sub> production and loss in the Martian atmosphere (the “stability of CO<sub>2</sub>”) is thought to be maintained by a HO<sub>x</sub>-catalyzed CO oxidation scheme [McElroy and Donahue, 1972; Parkinson and Hunten, 1972]. Thus, the rate of CO oxidation is sensitive to the abundance and altitude-distribution of the HO<sub>x</sub> species (OH, H and HO<sub>2</sub>).

Recent models of gas-phase chemistry in the Martian atmosphere predict ratios of CO to CO<sub>2</sub> lower than those observed, presumably due to an overabundance of HO<sub>x</sub> [Shimazaki, 1989; Krasnopolsky, 1991; Nair et al., 1991, 1992]. This is largely the result of two important factors which were not considered in the classic explanations of CO<sub>2</sub> stability [McElroy and Donahue, 1972; Parkinson and Hunten, 1972]. First, the temperature dependence of the CO<sub>2</sub> absorption cross section [e.g., DeMore and Patapoff, 1972; Lewis and Carver, 1983] was not accounted for in earlier studies. This effect should decrease the calculated CO<sub>2</sub> photolysis rate, while increasing the rate of HO<sub>x</sub> production via photolysis of H<sub>2</sub>O [Parisot and Zucconi, 1984; Anbar et al., this issue]. Second, the water vapor profiles used in most of the earlier Mars models assumed that water was present primarily near the surface (the lower 5–10 km). In current models, the lower atmosphere is considered well-mixed with respect to water to altitudes as high as 20–40 km, consistent with observational data [Jakosky and Farmer, 1982; Clancy et al., 1992]. This increases the amount of H<sub>2</sub>O exposed to photolysis at higher altitudes, thereby raising the rate of HO<sub>x</sub> production.

In a recent study which accounted for these factors, Shimazaki [1989] was able to balance CO<sub>2</sub> production and loss only by imposing an upper limit on the water vapor abundance of 1–2 precipitable microns (pr<sub>μm</sub>). This constraint limits the abundance of HO<sub>x</sub> species, which are largely derived from photolysis of H<sub>2</sub>O. However, this water vapor abundance is an order of magnitude lower than the globally averaged abundance measured by Viking [Jakosky and Farmer, 1982], and is also substantially lower than the recent measurements of Clancy et al. [1992].

The adsorption of HO<sub>x</sub> on aerosol surfaces is an alternative means of reducing HO<sub>x</sub> abundances [Anbar et al., 1991; Krasnopolsky et al., 1991]. Most Martian atmospheric models have assumed that HO<sub>x</sub> abundances are governed entirely by gas-phase chemistry [e.g., Yung et al., 1988; Shimazaki, 1989]. However, it is well established that reactive HO<sub>x</sub> radicals are adsorbed by a wide variety of surfaces (Table 1). Adsorption of these species on the surfaces of Martian aerosols could decrease HO<sub>x</sub> abundances significantly, thereby retarding CO oxidation.

Previous discussions of the influence of heterogeneous chemistry on the Martian atmosphere have largely focussed on heterogeneous catalysis of CO oxidation [e.g., Clark, 1971; Huguenin et al., 1977; Atreya and Blamont, 1990; Leu et al., 1992], although surface catalyzed CO oxidation has not yet been observed under Martian atmospheric conditions. HO<sub>x</sub> adsorption has typically been overlooked, although this phenomenon has been studied in the laboratory at temperatures and pressures approaching those of the lower Martian atmosphere (Table 1). Hunten [1974] was the first to suggest that “cold trapping” of water and HO<sub>x</sub> species on surfaces could strongly perturb gas-phase HO<sub>x</sub> catalytic chemistry. However, this was discussed as a low-temperature equilibrium condensation process, rather than as an adsorption reaction governed by the kinetics of gas-surface reactions, capable of occurring at temperatures typical of the Martian surface and lower atmosphere. Kong and McElroy [1977] made the only attempt to quantitatively consider the impact of heterogeneous destruction of HO<sub>x</sub>, but consid-

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TABLE 1. Surface Loss Coefficients on Inorganic Oxides

Surface	$\gamma$	T, K	Reference
<u>H Atom</u>			
H <sub>2</sub> O (s; amorphous)	> 0.1	< 150	1*
K <sub>2</sub> CO <sub>3</sub>	0.039	298	8
NaNO <sub>3</sub>	0.013	298	8
Pyrex	6.0x10 <sup>-3</sup>	298	3
Quartz	2.8x10 <sup>-3</sup>	298	3
PbO	1.9x10 <sup>-3</sup>	298	2
ZnO	1.2x10 <sup>-3</sup>	298	2
Cr <sub>2</sub> O <sub>3</sub>	1x10 <sup>-3</sup>	298	2
H <sub>2</sub> O (s)	1.6x10 <sup>-4</sup>	253	4
MgO	1x10 <sup>-4</sup>	298	2
H <sub>2</sub> SO <sub>4</sub>	≤ 5x10 <sup>-5</sup>	298	4
<u>OH Radical</u>			
H <sub>2</sub> SO <sub>4</sub>	1	298	4
H <sub>2</sub> O (s)	≥ 0.4	250	4
Fe(NO <sub>3</sub> ) <sub>3</sub> - FeO <sub>x</sub>	0.4	298	8
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.24	298	8
Al <sub>2</sub> O <sub>3</sub> (on Al metal)	0.10	250	4
FeSO <sub>4</sub> • nH <sub>2</sub> O	0.12	298	8
H <sub>2</sub> SO <sub>4</sub> (28 wt.%)	> 0.08	249	5
Zn(NO <sub>3</sub> ) <sub>2</sub>	0.045	298	8
FeO <sub>x</sub> (on steel)	0.04	250	4
NaNO <sub>3</sub>	0.036	298	8
Quartz	6.3x10 <sup>-3</sup>	250	4
H <sub>2</sub> O (l)	> 3.5x10 <sup>-3</sup>	275	5
<u>HO<sub>2</sub> Radical</u>			
H <sub>2</sub> O (l)	0.2	298	7
H <sub>2</sub> SO <sub>4</sub> (28 wt.%)	> 0.05	249	5
H <sub>2</sub> O (l)	> 0.01	275	5
Stainless Steel	1.7x10 <sup>-2</sup>	320	6
Glass	8x10 <sup>-3</sup>	298	6
FeO <sub>x</sub> (on steel)	3x10 <sup>-3</sup>	298	9
Quartz	4x10 <sup>-3</sup>	298	6

References: 1, *Buch and Zhang* [1991]; 2, *Thrush* [1965]; 3, *Wood and Wise* [1962]; 4, *Gershenson et al.* [1986]; 5, *Hanson et al.* [1992]; 6, *Gershenson and Purnal* [1990]; 7, *Mozurkewich et al.* [1987]; 8, *Jech et al.* [1982]; 9, *Rozhenshtein et al.* [1985].

\*Theoretical value.

ered only adsorption on the regolith at the Martian surface; reactions on aerosol surfaces (dust or ice) were not included, although the surface area available for reaction on aerosol particles in the Martian atmosphere is often comparable to the area of the planet's surface. Their study also did not account for the temperature-dependence of the CO<sub>2</sub> absorption cross section, and assumed that water in the atmosphere was present only very close to the surface.

In this study, we explore the suggestion that the adsorption and reaction of HO<sub>x</sub> on aerosol surfaces is an alternative mechanism for suppressing HO<sub>x</sub> abundances and retarding the rate of CO oxidation, without violating observational constraints on the abundance of H<sub>2</sub>O. Our intent is not to rigorously quantify the effects on CO chemistry, but to determine the feasibility of heterogeneous chemistry as a significant HO<sub>x</sub>-suppression mechanism. We assess the potential impact of heterogeneous processes involving the Martian surface, as well as dust and ice aerosols, on the abundance and altitude distributions of HO<sub>x</sub> species. The effects of these processes are compared to those of lowering the H<sub>2</sub>O abundance, and the implications for CO<sub>2</sub> chemistry are discussed.

#### MODEL DESCRIPTION

The potential impact of HO<sub>x</sub> adsorption was assessed by calculating HO<sub>x</sub> altitude profiles in the presence of ice and/or dust using a one dimensional photochemical model, including transport. The

Caltech/Jet Propulsion Laboratory generalized planetary atmosphere photochemistry code is described elsewhere [*Allen et al.*, 1981]. The model used here is a modified version of the model of *Yung et al.* [1988]. Details of this Mars model are described below.

#### Heterogeneous Chemistry

The rate of each HO<sub>x</sub> adsorption reaction was set equal to the collision frequency of the reacting species with a surface, multiplied by a surface loss coefficient,  $\gamma$ , which represents the fraction of collisions which result in loss of the species from the gas phase ( $0 < \gamma < 1$ ). Published measurements of  $\gamma$  for HO<sub>x</sub> species are summarized in Table 1, and discussed further below. The collision frequency of a gas-phase species with an aerosol surface at a given altitude is a function of the mean thermal molecular speed ( $v$ ; cm s<sup>-1</sup>), and the surface area ( $S$ ; cm<sup>2</sup>/cm<sup>3</sup>) available at that altitude, following the equation:

$$\text{Rate (cm}^{-3} \text{ s}^{-1}) = (1/4) \gamma S v N_i,$$

where  $N_i$  (cm<sup>-3</sup>) is the number density of the species being adsorbed [*Michelangelo et al.*, 1991]. The temperatures used to calculate  $v$  are described below. The dust and ice surfaces available for reaction in the model are plotted in Figure 1 as extinction coefficients ( $\tau$ ). For spherical particles, surface area and extinction coefficient are approximately related by  $S = 2\tau$ , assuming that the optical cross section is equal to twice the geometrical cross section.

For dust, the available surface area was calculated from dust distributions and particle dimensions supplied by D. Michelangelo, based on the work of *Michelangelo et al.* [in press]. An overall optical depth of approximately 0.2 was assumed; this represents a relatively clear Martian atmosphere, and does not simulate the much higher opacities observed during global dust storms. These data are similar to those obtained by Phobos 2 [*Blamont et al.*, 1991]. We note that the total surface area available for reaction on these particles is comparable to the area of the planet's surface.

Persistent, geographically extensive detached hazes of water ice are common in the Martian atmosphere [e.g., *Kahn*, 1990]. Two different ice distribution profiles were included in this study, because these hazes have been observed over a range of altitudes. The first profile, based on data supplied by D. Michelangelo, reaches a maximum ice abundance at 30 km. The second profile assumes the same distribution, but shifted 20 km higher to match observations by Phobos 2 [*Blamont et al.*, 1991].

Once adsorbed, HO<sub>x</sub> species are assumed to react with gas phase OH or H, resulting in conversion to H<sub>2</sub>O or H<sub>2</sub>, which are rapidly returned to the gas phase. This mechanism is necessary to preserve mass balance and maintain the overall oxidation state of the atmos-

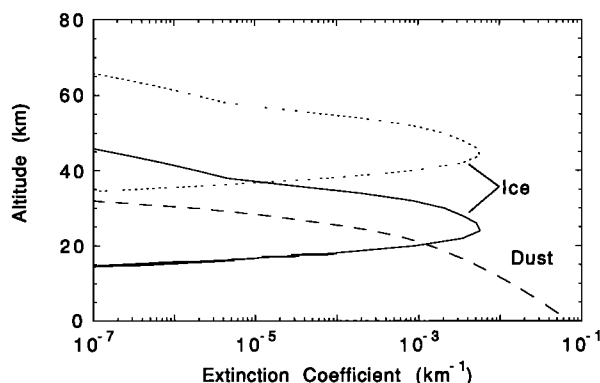
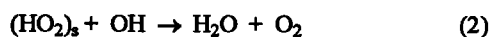


Fig. 1. Extinction coefficients of ice haze at 30 km (solid line), ice haze at 50 km (dotted line), and dust (dashed line). A total optical depth of  $\approx 0.2$  due to dust is assumed.

phere. For example, in the case of HO<sub>2</sub> adsorption (H and OH adsorption can be treated similarly), the surface chemistry is parameterized as



where (HO<sub>2</sub>)<sub>s</sub> denotes the adsorbed species. At steady state, the rate of the net reaction must equal the rate of reaction (1). Thus, surface chemistry can be thought of as catalyzing the destruction of HO<sub>x</sub>.

### Homogeneous Chemistry

We have considered the gas phase chemistry of a CO<sub>2</sub>-H<sub>2</sub>O atmosphere. The continuity equation, including transport, was

solved for the species CO<sub>2</sub>, CO, O<sub>2</sub>, O, O(<sup>1</sup>D), O<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, OH, HO<sub>2</sub>, H<sub>2</sub>, and H. The gas-phase reactions incorporated in the model and their rate constants are listed in Table 2. Rate constants for three-body reactions were increased by a factor of two from the tabulated values to account for the efficiency of CO<sub>2</sub> as a third body [Yung and DeMore, 1982].

### Boundary Conditions

In our model calculations, the number densities of O<sub>2</sub>, CO and CO<sub>2</sub> at 0 km were fixed to observed values (2.34 × 10<sup>14</sup> cm<sup>-3</sup>, 1.26 × 10<sup>14</sup> cm<sup>-3</sup>, and 2.05 × 10<sup>17</sup> cm<sup>-3</sup>, respectively). The abundance of H<sub>2</sub>O was also fixed at the ground. Two H<sub>2</sub>O cases were modeled; one with an integrated column abundance of 16 prμm, and the other with 1.6 prμm. Following Shimazaki [1989], H<sub>2</sub>O was modeled as well-mixed up to a "critical altitude," above which saturation was assumed. The height of the critical altitude is determined by the

TABLE 2. Gas-Phase Reactions in the Martian Atmosphere

	Reaction	Rate Coefficient <sup>a</sup>	Reference
R1a	O <sub>2</sub> + <i>hν</i> → 2O	1.1 × 10 <sup>-7</sup>	§
R1b	→ O + O( <sup>1</sup> D)	6.8 × 10 <sup>-7</sup>	§
R2a	O <sub>3</sub> + <i>hν</i> → O <sub>2</sub> + O	3.3 × 10 <sup>-4</sup>	§
R2b	→ O <sub>2</sub> + O( <sup>1</sup> D)	2.1 × 10 <sup>-3</sup>	§
R3a	H <sub>2</sub> O + <i>hν</i> → H + OH	2.7 × 10 <sup>-6</sup>	§
R3b	→ H <sub>2</sub> + O( <sup>1</sup> D)	1.7 × 10 <sup>-7</sup>	§
R3c	→ 2H + O	2.0 × 10 <sup>-7</sup>	§
R4	H <sub>2</sub> O <sub>2</sub> + <i>hν</i> → 2OH	2.9 × 10 <sup>-5</sup>	§
R5a	CO <sub>2</sub> + <i>hν</i> → CO + O	3.7 × 10 <sup>-7</sup>	§
R5b	→ CO + O( <sup>1</sup> D)	1.4 × 10 <sup>-7</sup>	§
R6	2O + M → O <sub>2</sub> + M	4.3 × 10 <sup>-28</sup> T <sup>-2.00</sup>	1
R7	2O + O <sub>2</sub> → O <sub>3</sub> + O	6.4 × 10 <sup>-35</sup> e <sup>663/T</sup>	2
R8	O + O <sub>2</sub> + CO <sub>2</sub> → O <sub>3</sub> + CO <sub>2</sub>	5.0 × 10 <sup>-35</sup> e <sup>724/T</sup>	2
R9	O + O <sub>3</sub> → 2O <sub>2</sub>	8.0 × 10 <sup>-12</sup> e <sup>-2060/T</sup>	3
R10	O + CO + M → CO <sub>2</sub> + M	6.5 × 10 <sup>-33</sup> e <sup>-2184/T</sup>	4
R11	O( <sup>1</sup> D) + O <sub>2</sub> → O + O <sub>2</sub>	3.2 × 10 <sup>-11</sup> e <sup>70/T</sup>	3
R12a	O( <sup>1</sup> D) + O <sub>3</sub> → 2O <sub>2</sub>	1.2 × 10 <sup>-10</sup>	3
R12b	→ O <sub>2</sub> + 2O	1.2 × 10 <sup>-10</sup>	3
R13	O( <sup>1</sup> D) + H <sub>2</sub> → H + OH	1.0 × 10 <sup>-10</sup>	3
R14	O( <sup>1</sup> D) + CO <sub>2</sub> → O + CO <sub>2</sub>	7.4 × 10 <sup>-11</sup> e <sup>120/T</sup>	3
R15	O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH	2.2 × 10 <sup>-10</sup>	3
R16	2H + M → H <sub>2</sub> + M	1.5 × 10 <sup>-29</sup> T <sup>-1.30</sup>	5
R17	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	k <sub>0</sub> = 5.2 × 10 <sup>-28</sup> T <sup>-1.60</sup> k <sub>∞</sub> = 7.5 × 10 <sup>-11</sup>	3
R18	H + O <sub>3</sub> → OH + O <sub>2</sub>	1.4 × 10 <sup>-10</sup> e <sup>-470/T</sup>	3
R19a	H + HO <sub>2</sub> → 2OH	6.8 × 10 <sup>-11</sup>	6
R19b	→ H <sub>2</sub> + O <sub>2</sub>	2.9 × 10 <sup>-12</sup>	6
R19c	→ H <sub>2</sub> O + O	1.4 × 10 <sup>-12</sup>	6
R20	O + H <sub>2</sub> → OH + H	1.6 × 10 <sup>-11</sup> e <sup>-4570/T</sup>	1
R21	O + OH → O <sub>2</sub> + H	2.2 × 10 <sup>-11</sup> e <sup>120/T</sup>	3
R22	O + HO <sub>2</sub> → OH + O <sub>2</sub>	3.0 × 10 <sup>-11</sup> e <sup>200/T</sup>	3
R23	O + H <sub>2</sub> O <sub>2</sub> → OH + HO <sub>2</sub>	1.4 × 10 <sup>-12</sup> e <sup>-2000/T</sup>	3
R24	2OH → H <sub>2</sub> O + O	4.2 × 10 <sup>-12</sup> e <sup>-240/T</sup>	3
R25	2OH + M → H <sub>2</sub> O <sub>2</sub> + M	k <sub>0</sub> = 6.6 × 10 <sup>-29</sup> T <sup>-0.80</sup> k <sub>∞</sub> = 1.5 × 10 <sup>-11</sup>	3
R26	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	1.6 × 10 <sup>-12</sup> e <sup>-940/T</sup>	3
R27	OH + H <sub>2</sub> → H <sub>2</sub> O + H	5.5 × 10 <sup>-12</sup> e <sup>-2000/T</sup>	3
R28	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	4.8 × 10 <sup>-11</sup> e <sup>230/T</sup>	3
R29	OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	3.3 × 10 <sup>-12</sup> e <sup>-200/T</sup>	3
R30	OH + CO → CO <sub>2</sub> + H	1.5 × 10 <sup>-13</sup> (1 + 0.6P <sub>atm</sub> )	3
R31	HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	1.1 × 10 <sup>-14</sup> e <sup>-500/T</sup>	3
R32	2HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	2.3 × 10 <sup>-13</sup> e <sup>600/T</sup>	3
R33	2HO <sub>2</sub> + M → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> + M	1.7 × 10 <sup>-33</sup> e <sup>1000/T</sup>	3

References: 1, Hampson [1980]; 2, Lin and Leu [1982]; 3, Demore et al. [1990]; 4, Baulch et al. [1976]; 5, Tsang and Hampson [1986]; 6, Yung et al. [1988].

<sup>§</sup> Cross sections used to calculate photodissociation rate constants for CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O are described in Anbar et al. [this issue]. Cross sections for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> photodissociation calculations are similar to those used in Yung et al. [1988].

<sup>a</sup>Units are s<sup>-1</sup> for photolysis reactions, cm<sup>3</sup> s<sup>-1</sup> for two-body reactions, and cm<sup>6</sup> s<sup>-1</sup> for three-body reactions. Photolysis rate constants refer to the optically thin region. Reactions with CO<sub>2</sub> as a third body have had their rate constants increased by a factor of two from the values given here.

H<sub>2</sub>O column abundance. In our 16  $\mu\text{m}$  and 1.6  $\mu\text{m}$  models, the critical heights were  $\approx 20$  km and 35 km, respectively. The two H<sub>2</sub>O profiles, shown in Figure 2, are in agreement with those of Shimazaki [1989] below 50 km, but are somewhat larger at higher altitudes.

Following Yung *et al.* [1988], the escape velocities of H and H<sub>2</sub> were fixed to  $6.76 \times 10^3 \text{ cm s}^{-1}$  and  $1.70 \times 10^2 \text{ cm s}^{-1}$ . The O escape flux was set to  $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ , in agreement with McElroy [1972].

#### Other Input Parameters

The eddy diffusivity profile in the Martian atmosphere is uncertain, and has been the subject of some debate [e.g., Kong and McElroy, 1977; Kahn, 1990; Atreya and Blamont, 1990]. Our results should be insensitive to this profile, over the range of values that has been suggested. This is due to the exceedingly short lifetimes of the HO<sub>x</sub> species relative to the transport timescale. At the ground, the lifetime of the HO<sub>x</sub> family is on the order of  $[\text{HO}_x]/k_{28}[\text{OH}][\text{HO}_2] \approx 10^4 \text{ s}$ , while the transport timescale can be approximated by  $H^2/K_z$  ( $H$  is atmospheric scale height;  $K_z$  is eddy diffusivity)  $\approx 10^{12}/10^5 = 10^7 \text{ s}$ . Therefore, the HO<sub>x</sub> family is in a state of photochemical equilibrium. The abundances of longer-lived species (e.g., CO and O<sub>2</sub>) which could be impacted by different eddy diffusivity profiles, and hence affect the partitioning of the HO<sub>x</sub> species, have been fixed to observed values. Thus, the distribution of the HO<sub>x</sub> species should be independent of the choice of the eddy diffusion profile. The eddy diffusion coefficients used in this model grade exponentially from  $10^5 \text{ cm}^2 \text{ s}^{-1}$  at the surface to  $5 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$  at 100 km, and remain constant at higher altitudes. This is similar to Shimazaki's [1989] profile A.

The COSPAR temperature profile has been adopted below 100 km [Seiff, 1982], with an exospheric temperature of 365 K [Kong and McElroy, 1977]. The temperature profile of the upper atmosphere was then found by fitting a spline curve to these data.

Solar flux values at 1 AU were obtained from Mount and Rottman [1983] and Torr and Torr [1985], and scaled to 1.52 AU. The cross sections used to calculate photodissociation rate constants are described in Anbar *et al.* [this issue] and Yung *et al.* [1988]. CO<sub>2</sub> cross sections were adopted from Lewis and Carver [1983], and the temperature dependence of CO<sub>2</sub> absorption was modeled following the procedure of Anbar *et al.* [this issue]. No adjustment was made for aerosol scattering or absorption in the results presented below. We find that incorporation of these effects into the model changes photolytic rate constants by a maximum amount of 10–20% at the ground. The magnitude of this effect decreases with increasing altitude. Since the bulk of HO<sub>x</sub> formation occurs near 20 km, and since HO<sub>x</sub> lifetimes are very short with respect to transport times-

cales, aerosol effects on the radiation field should not have much impact on our results. All computations employed a diurnally averaged radiation field at equinox for  $\approx 30^\circ$  latitude.

#### MODEL RESULTS

HO<sub>x</sub> profiles were calculated for a number of different models (Table 3), and the results are summarized in Figures 3–6. Models A and B (Figure 3) invoke no heterogeneous chemistry, but assume water vapor abundances of 16 and 1.6  $\mu\text{m}$ , respectively. The results of model B are close to those of Shimazaki [1989], who also assumed  $\approx 1 \mu\text{m}$  H<sub>2</sub>O. The depletions of HO<sub>2</sub>, H and OH in model B relative to model A are largest in the lower atmosphere (below 50 km), since the largest differences in water vapor abundances occur near the surface (Figure 2), and the chemical loss timescales for these species dominate over transport timescales. The abundances of OH and HO<sub>2</sub> are most strongly affected; their column densities are depleted by  $\approx 25\%$  and  $\approx 65\%$ , respectively. Significantly, in both models, HO<sub>2</sub> is the dominant HO<sub>x</sub> species between the ground and  $\approx 35$  km, which is where most of the dust surface area is available. This is also where most of the ice surface is available in the low-altitude ice haze case we have considered (Figure 1). At higher altitudes, where the ice abundance may exceed that of dust (Figure 1), H is the primary HO<sub>x</sub> species. Thus, the influence of HO<sub>x</sub> adsorption is determined by the rate of adsorption of HO<sub>2</sub> on dust and regolith, and on low-altitude ice, and of H on ice at higher altitudes; the rate of adsorption of OH on either surface is insignificant by comparison. Due to the reactions which relate the HO<sub>x</sub> radicals to one another, heterogeneous loss of one of these radicals propagates through the entire HO<sub>x</sub> family.

Heterogeneous chemistry was incorporated in models C1, C2, C3, D1, D2, E1, E2 and E3, all of which assumed 16  $\mu\text{m}$  of water vapor. Adsorption on dust and on the surface (C1, C2 and C3) was considered separately from adsorption on ice (D1, D2, E1, E2 and E3) to allow the effects of reactions on different surfaces to be distinguished. In models C1, C2, C3, D1 and D2, only HO<sub>2</sub> adsorption was considered. Models E1, E2 and E3 include only H adsorption. Since gas-phase HO<sub>x</sub>-catalyzed CO oxidation is most rapid below 40 km [e.g., Kong and McElroy, 1977; Shimazaki, 1989], the impact of heterogeneous HO<sub>x</sub> depletion on CO chemistry can be assessed to first order by comparing the HO<sub>x</sub> altitude distributions to this 40 km "threshold." The abundance of OH is particularly critical, since the rate of CO oxidation is limited by the rate of  $\text{R30}$  ( $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ).

Examination of the C models (Figure 4) reveals that adsorption of HO<sub>2</sub> on dust can significantly deplete some HO<sub>x</sub> species in the lower atmosphere, even for  $\gamma_{\text{HO}_2} = 0.001$  (model C1). If  $\gamma_{\text{HO}_2} = 0.01$ , the total HO<sub>x</sub> budget in model C2 approaches that of the 1.6  $\mu\text{m}$  water vapor case (model B). Although the abundance of OH is only reduced by  $\approx 10\%$  on a column-integrated basis (Table 3), the bulk of this reduction occurs below 20 km, where the rate of HO<sub>x</sub>-catalyzed CO recombination is highest when heterogeneous chemistry is not included. Thus, the rate of CO recombination may be retarded substantially by adsorption of HO<sub>2</sub> on dust, with  $\gamma_{\text{HO}_2} = 0.01$ . If an even larger surface loss coefficient is considered ( $\gamma_{\text{HO}_2} = 0.1$ ; model C3), then the total HO<sub>x</sub> abundance is actually lowered below that of model B, and the OH abundance comes within 25% of model B. The plausibility of these values of  $\gamma$  is assessed below.

Adsorption of HO<sub>2</sub> on ice particles centered at 30 km was considered in models D1 and D2 (Figure 5), while adsorption of H on a haze at 50 km was considered in models E1, E2 and E3 (Figure 6). Adsorbed H was assumed to react with gas-phase H to produce H<sub>2</sub> gas, by analogy with the HO<sub>2</sub> surface chemistry described earlier. The influence of ice surfaces on HO<sub>x</sub> abundances, as

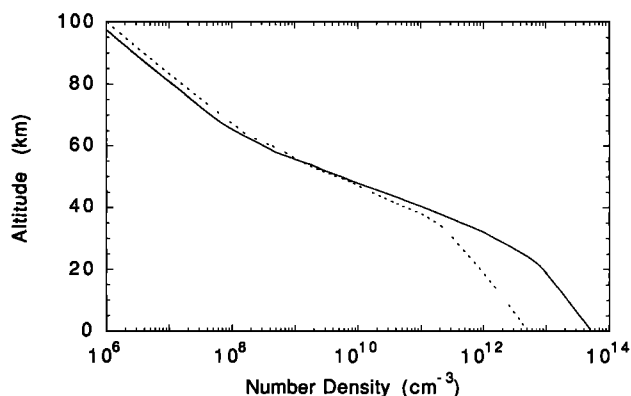
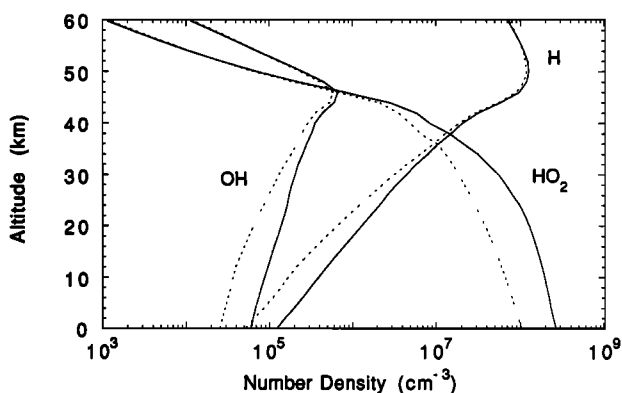
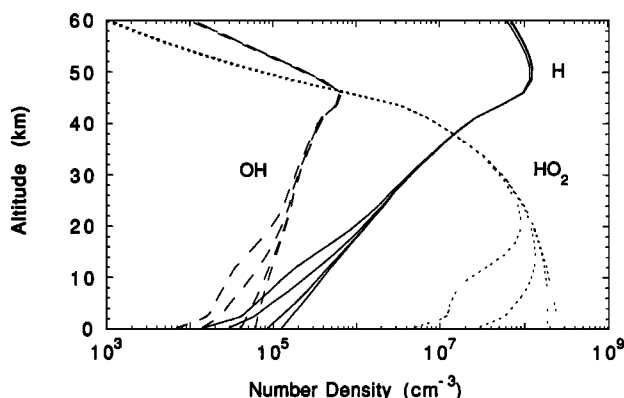


Fig. 2. H<sub>2</sub>O profiles corresponding to globally averaged water vapor abundances of 16  $\mu\text{m}$  (solid line) and 1.6  $\mu\text{m}$  (dotted line).

TABLE 3. Summary of Model Results: HO<sub>x</sub> Column Abundances

Model	H <sub>2</sub> O pr $\mu$ m	Surfaces	$\gamma$	H $\times 10^{14}$	OH $\times 10^{12}$	HO <sub>2</sub> $\times 10^{14}$	$\Sigma$ HO <sub>x</sub> $\times 10^{14}$
A	16	—	—	2.58	1.20	5.05	7.64
B	1.6	—	—	2.51	0.88	1.74	4.25
C1	16	Dust and Regolith	$\gamma_{\text{HO}_2} = 0.001$	2.58	1.17	4.56	7.15
C2	16	Dust and Regolith	$\gamma_{\text{HO}_2} = 0.01$	2.52	1.10	3.20	5.75
C3	16	Dust and Regolith	$\gamma_{\text{HO}_2} = 0.1$	2.36	1.00	1.76	4.13
D1	16	Ice at 30 km	$\gamma_{\text{HO}_2} = 0.01$	2.58	1.19	4.98	7.57
D2	16	Ice at 30 km	$\gamma_{\text{HO}_2} = 0.1$	2.48	1.08	4.45	6.94
E1	16	Ice at 50 km	$\gamma_{\text{H}} = 0.001$	2.30	1.11	5.06	7.37
E2	16	Ice at 50 km	$\gamma_{\text{H}} = 0.01$	1.21	0.86	5.03	6.25
E3	16	Ice at 50 km	$\gamma_{\text{H}} = 0.1$	0.71	0.74	5.01	5.72

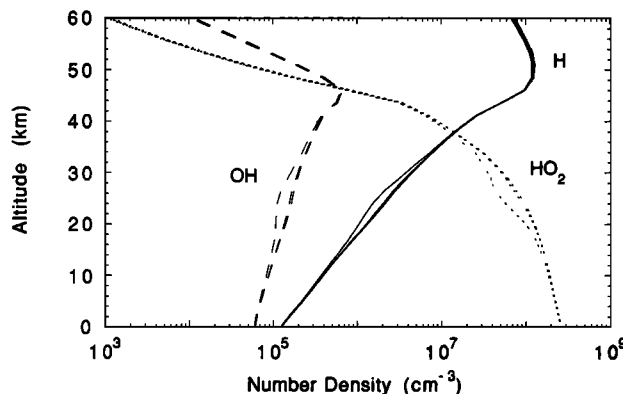
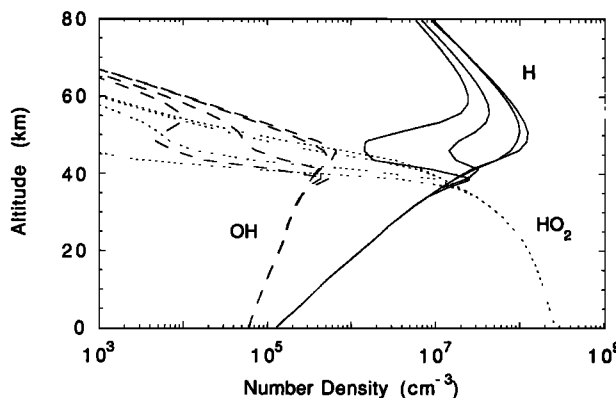
Abundances of H, OH, HO<sub>2</sub> and  $\Sigma$ HO<sub>x</sub> reported as cm<sup>-2</sup>Fig. 3. Distribution of HO<sub>x</sub> species calculated for model A (solid line) and model B (dotted line).Fig. 4. Distribution of HO<sub>2</sub> (dotted line), H (solid line), and OH (dashed line) in models A, C1, C2, and C3. The highest abundances for all three species are those of model A. Abundances decrease as  $\gamma_{\text{HO}_2}$  increases from 0.001 (model C1) to 0.1 (model C3). A water vapor abundance of 16 pr $\mu$ m is assumed.

expected, is very sensitive to the altitude of the ice cloud. When the ice distribution is centered at 30 km and  $\gamma_{\text{HO}_2} = 0.01$  (model D1), only a very small impact on HO<sub>x</sub> is seen in the lower atmosphere. Values of  $\gamma_{\text{HO}_2}$  on the order of 0.1 (model D2) are necessary to achieve an OH abundance comparable to that of model C2. Even higher values would be necessary to approach the depletions found in the case of low water abundance (model B). The inclusion of H adsorption on ice in the lower atmosphere was found to have little effect on HO<sub>x</sub> abundances.

If the ice distribution maximum is shifted to  $\approx 50$  km (models E1, E2 and E3), the predicted abundances of H and OH are substantially

smaller than in the 30 km cases utilizing comparable values of  $\gamma$  (e.g. compare models D1 and E2, or D2 and E3). Even if  $\gamma_{\text{H}} = 0.001$  (model E1), OH is depleted by nearly 10% relative to model A. The sensitivity to the altitude distribution of the ice particles is due largely to the fact that, in the purely gas-phase case, the chemical loss timescale of OH (and, hence, its abundance) has a maximum near 50 km. Thus, the introduction of a heterogeneous loss process has its greatest effect on OH at this altitude.

Of all the heterogeneous cases studies, models E2 and E3 have the largest impact on the OH abundance, resulting in even lower

Fig. 5. Distribution of HO<sub>2</sub> (dotted line), H (solid line) and OH (dashed line) in models A, D1, and D2. The highest abundances for all three species are those of model A. Abundances decrease as  $\gamma_{\text{HO}_2}$  increases from 0.01 (model D1) to 0.1 (model D2). A water vapor abundance of 16 pr $\mu$ m is assumed.Fig. 6. Distribution of HO<sub>2</sub> (dotted line), H (solid line), and OH (dashed line) in models A, E1, E2, and E3. The highest abundances for all three species are those of model A. Abundances decrease as  $\gamma_{\text{H}}$  increases from 0.001 (model E1) to 0.1 (model E3). A water vapor abundance of 16 pr $\mu$ m is assumed.

abundances than in model B. However, due to the ice particle distribution, this depletion occurs primarily above 40 km (Figure 5), where the rate of HO<sub>x</sub>-catalyzed CO recombination is quite low [e.g., Kong and McElroy, 1977; Shimazaki, 1989]. Thus, heterogeneous processes on ice surfaces at these altitudes are likely to have only a small effect on CO<sub>2</sub> stability.

#### COMPARISONS WITH LABORATORY ADSORPTION DATA

The plausibility of the range of  $\gamma$  values described above can only be assessed by making comparisons to laboratory data. Unfortunately, the number of studies of HO<sub>x</sub> adsorption is small, and most surfaces that have been studied are not directly relevant to the Martian surface or aerosols. They are, at best, crude analogs of the reactive surfaces available on Mars, which are likely to be composed of complex, iron-rich oxide and silicate weathering products of basalts [e.g., Bell *et al.*, 1990; Morris *et al.*, 1990; Pinet and Chevreil, 1990]. Nonetheless, we believe the published data are useful to provide order-of-magnitude estimates of  $\gamma$ .

Table 1 summarizes the published values of HO<sub>x</sub> surface loss coefficients on inorganic oxides. HO<sub>x</sub> adsorption data on metal surfaces have not been included, although these tend to be substantially larger than the values on oxides [e.g., Thrush, 1965]. We have also omitted data from early studies which indicate relatively large values of  $\gamma_{\text{HO}_2}$  on oxide surfaces [e.g., Smith, 1943]; we are not confident of the reliability of these early measurements.

Most data were collected at or near room temperature. At lower temperatures, it is expected that  $\gamma$  should increase. This can be understood if the data represent an equilibrium between an energetically favorable adsorption reaction, and an endothermic desorption process. Such behavior has been observed for OH and HO<sub>2</sub> on H<sub>3</sub>PO<sub>4</sub>, where loss coefficients increase by an order of magnitude as temperature is lowered from 298 K to 220 K [Margitan, 1976; Howard, 1979]. This observation is of special importance to the Martian atmosphere, where typical temperatures are < 220 K.

The HO<sub>2</sub> data demonstrate that a  $\gamma_{\text{HO}_2}$  value > 0.001 is entirely consistent with the few studies that have been done. A value of 0.01 on potential Martian surfaces is plausible if temperature effects are considered (see above). This conclusion is strengthened if the OH data are considered. Although adsorption of OH is probably not an important HO<sub>x</sub> sink in the Martian atmosphere, we include these data because OH and HO<sub>2</sub> have similar affinities for many surfaces [Jech *et al.*, 1982]; in Table 1,  $\gamma_{\text{OH}}$  and  $\gamma_{\text{HO}_2}$  are typically within an order of magnitude of each other for comparable surfaces. Moreover, the OH data are the most comprehensive, since they cover a variety of complex oxides, including some containing iron. If the OH data are used to supplement the HO<sub>2</sub> data by inference, then  $\gamma_{\text{HO}_2} \approx 0.01$  seems a reasonable estimate for adsorption on Martian dust and regolith, particularly at low temperatures. Higher values of  $\gamma$  are possible, but are not well supported by the laboratory data. The adsorption affinity of HO<sub>2</sub> for ice is unknown, but is likely to be  $\geq 0.01$  on the basis of comparison with data for adsorption on liquid water, as well as the OH data. A value as high as  $\gamma_{\text{HO}_2} \approx 0.1$  is plausible.

The adsorption of H on ice is more problematic. The only laboratory study indicates  $\gamma_{\text{H}} < 0.001$  [Gershenzon *et al.*, 1986], which is too small for an appreciable effect in the atmosphere. However, a theoretical study of adsorption on amorphous ice suggests  $\gamma_{\text{H}} > 0.1$  at < 150 K [Buch and Zhang, 1991]. The applicability of this result to Martian ice surfaces is doubtful, since typical Martian atmospheric temperatures are higher than those at which amorphous ice is stable. Thus, the adsorption of H is unlikely to be an important process.

#### DISCUSSION AND CONCLUSIONS

Our findings indicate that heterogeneous chemistry on aerosols is capable of lowering the abundance of HO<sub>x</sub> species in the Martian atmosphere. Adsorption of HO<sub>2</sub> on either dust or ice surfaces below 40 km could have a non-trivial impact on the abundance of HO<sub>x</sub>, and hence on the ratio of CO : CO<sub>2</sub>; the predicted depletions of OH ( $\approx 10\%$  or more) approach those achieved by lowering the H<sub>2</sub>O abundance from 16 ppm to 1.6 ppm ( $\approx 25\%$ ), which could significantly retard the rate of CO oxidation. The  $\gamma$  values required for such an effect ( $\gamma_{\text{HO}_2} \geq 0.01$  on dust;  $\gamma_{\text{HO}_2} \geq 0.1$  on ice) are not unreasonable when compared to the few laboratory data available. However, there is a clear need for laboratory experiments on surfaces representative of Martian aerosols, and at temperatures approaching those of the lower Martian atmosphere.

Adsorption of H on ice near 50 km altitude can also result in substantial HO<sub>x</sub> depletions, if  $\gamma_{\text{H}} \geq 0.01$ . However, these depletions are confined to altitudes at which the rate of HO<sub>x</sub>-catalyzed CO oxidation is already low. Additionally, these values of  $\gamma_{\text{H}}$  are higher than observed in the only relevant laboratory study. Thus, little impact on the chemistry of CO is expected from H adsorption on ice.

While this study has demonstrated the potential influence of heterogeneous chemistry, a critical re-examination of Martian atmospheric chemistry is required to rigorously quantify the importance of such reactions. For example, the uncertainties associated with some of the rate constants used in this model are as large as  $\pm 30\%$  at room temperature, with somewhat higher uncertainties at Martian temperatures. Thus, it may be possible to reduce the abundance of HO<sub>x</sub> radicals in the modeled atmosphere by manipulating key rate constants within the reported uncertainties. The abundance of HO<sub>x</sub> is controlled by the rate of production, via H<sub>2</sub>O photolysis with a contribution from  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$  (R15) at the surface, and the rate of loss, dominated by the reaction  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  (R28). Thus, the abundance of HO<sub>x</sub> can be decreased by decreasing the production rate (R3a + K15 [ $\text{O}(^1\text{D})$ ] [ $\text{H}_2\text{O}$ ]), increasing the rate constant K28, or a combination of these changes. The impact of reasonable "re-evaluations" of these gas-phase data must be quantified.

Additionally, reactions involving HO<sub>x</sub> are considered critical to many processes in the Martian atmosphere (e.g., the abundance of O<sub>3</sub>, the escape rate of H, and the coupling of H escape to O escape). If HO<sub>x</sub> abundances must be suppressed, we may need to revise our explanations of the chemistry governing such processes. For example, although it is generally assumed that O<sub>3</sub> loss is dominated by reaction with HO<sub>x</sub> [e.g., Lindner, 1988], catalytic NO<sub>x</sub> chemistry may become important if HO<sub>x</sub> levels are depressed. Hence, the photochemistry of nitrogen [Yung *et al.*, 1977] should be re-examined in light of this work.

It must be realized that the inclusion of heterogeneous HO<sub>x</sub> chemistry introduces a complicated variable into Martian atmospheric modeling, since the altitude distributions of H, OH and HO<sub>2</sub> are sensitive to the altitude distribution of the aerosol surfaces (compare models C2, D1, and E2). Like the water vapor abundance, the altitude distribution of aerosol surfaces (especially ice surfaces) varies latitudinally, seasonally and diurnally. Thus, heterogeneous HO<sub>x</sub> chemistry must be introduced with care, and should not be used to "solve" modeling difficulties until all the reasonable permutations of gas-phase chemistry have been explored. Despite this caveat, the importance of quantifying the role of heterogeneous chemistry in the atmosphere of Mars cannot be overlooked. In the comparative planetology of atmospheres, Mars is said to possess the "dustiest" atmosphere. The impact of aerosols on Martian atmos-

pheric chemistry is largely unknown, despite some imaginative but unproven speculations [Huguenin, et al. 1977; Atreya and Blamont, 1990]. This study has combined laboratory data and photochemical modeling to demonstrate that heterogeneous chemistry could be important in regulating the abundance of HO<sub>x</sub>. This opens the exciting possibility that the Martian atmosphere may be a natural laboratory for the quantitative study of heterogeneous reactions, which are now considered important in the terrestrial atmosphere [Molina et al., 1987; Tolbert et al., 1988; Leu, 1988; Michelangeli et al., 1991].

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